

USES AND DEVELOPMENT OF WATER QUALITY MONITORING TECHNOLOGY

Jean Kozul and Lynn Haas, National Institute for Environmental Renewal¹

Alternative technologies for water quality monitoring were used to develop an integrated environmental monitoring and data management system for watershed assessments. The system includes a GIS watershed visualization, model analysis and a decision support tool for stakeholder watershed management. The program was funded by a grant through the US EPA. This describes our experiences with data quality using ion selective electrode (ISE) technology for screening dissolved oxygen (DO) and nitrate levels in-situ and our plans for future technology evaluations. We performed the water quality monitoring from 7/98 through 9/98 in the Wissahickon Watershed. The Wissahickon is a 64 sq.mi. urban/suburban watershed in southeastern Pennsylvania (PA), located in the PA Appalachian Piedmont physiographic province. It enters the Schuylkill River in Philadelphia.

The PADEP, the US EPA, and others performed investigations of the Wissahickon in the last decade. Studies indicated impaired aquatic habitats and high nutrient levels in the watershed. In a recent study, nitrate concentrations ranged from not detected to 8.9 mg/l (Boyer, 1997). In 1998, 6 segments of the mainstem (~18 mi.) and several tributaries (~16 mi.) were listed on the 1998 303(d) list. Among the sources and causes of impairments identified by the PADEP were nutrients from wastewater treatment plant point sources and urban runoff and storm sewer nonpoint sources.

Our water quality monitoring program was designed to measure conventional water quality parameters: temperature, pH, DO, conductivity and turbidity, using continuous monitoring technologies in order to assess diel DO at areas of suspected nutrient impairment. We also evaluated ISEs for nitrate and ammonia. Two rounds of stream samples were collected using US Geological Survey flow-weighted sample collection methods for conventional laboratory analysis.

In ISE analysis, the electric potential between a sensing and a reference electrode due to the activity of a specific ion is measured and related to the concentration of the ion species through the Nernst equation. The electrodes are calibrated to standards and react with the sample ion species. The sondes used in this study had combination electrodes. These water quality sondes do not have mechanisms for adding reagent treatments that enhance the specific ion activity responses and measurements to the samples and reference standards (Standard Methods, 1999, 20th Ed).

In order to collect useable data and be able to evaluate its accuracy and reliability, we performed extensive quality assurance/quality control (QA/QC). We used high quality state-of-the-art sensors, which were factory calibrated and checked before use. We verified the DO levels ~ every 48 hrs with calibrated field instruments and recalibrated the DO probe in the field. We verified the DO probe and field instruments measurements using the Winkler titration method. On a weekly basis, we brought the sondes into our field lab and checked the range of the measurements for all parameters using standards. The probes were recalibrated and the calibrations were verified against a second source of certified standards. We kept detailed field and laboratory logs of the QA/QC results.

Fig. 1 is a composite graph of the DO measurements collected by 6 sondes in 17 different locations. In two months, we encountered a few DO sensor membrane failures. The membranes were replaced and the sondes resumed collecting measurements. We compared the means and ranges of the sonde DO data to the DO data from the baseflow sampling. Fig. 2 shows the concentrations of DO measured in baseflow samples, plotted in a longitudinal profile along the mainstem. The 17 sonde locations were at or near baseflow sampling locations. Although the sondes were not in all these locations at the time of baseflow sampling, the mean plots of the sonde

¹ National Institute for Environmental Renewal, 1300 Old Plank Road, Mayfield, PA 18433
Telephone: (570) 282-0302 – Fax: (570) 282-3381 – email: jkozul@nier.org; lhaas@nier.org.

measurements showed good agreement with the baseflow measurements. Except for the occasional DO membrane failure, fouling caused by algal growth or debris getting caught in the sondes, there was consistent agreement between the calibrated field checks, performed ~ every two days and the sonde measurements. Fig. 3 illustrates the DO concentrations measured by a sonde every 15 minutes over the time it was in one location (L4) in the watershed and the field verifications. Based on the QA/QC data collected over the course of the study, we have a high level of confidence that the ISE technology used gave reliable, good quality DO data.

The ISE technology nitrate measurements collected in this study did not provide a high level of confidence for reliable, useable data. The results of the baseflow laboratory analyses indicated that the nitrate levels in the stream ranged from not detected to 20 mg/l at various sample locations (Fig. 4). Fig. 5 shows the results of all the nitrate measurements collected by the sondes during the study period. The scale of concentrations was plotted from 0 to 100 mg/l to show the majority of the sonde results. Some data were in the 1000's and 10,000's of mg/l and plot off this scale. Most were outside the range of results reported in the 1998 baseflow sampling (0-20 mg/l).

A comparison of the baseflow sample laboratory analytical results to the sonde screening results indicates close agreement of results in only two instances (Figs. 6 and 7). Relative percent differences (RPD) in the close instances are 49.3%, 11.3% and 37.2. In a fourth case, the lab result was 18 mg/l and the sonde read over 5500 mg/l. The baseflow program had a high degree of field and laboratory QA/QC checks (field and method blank, duplicate and replicate samples). The reported results met all data quality objectives and are considered reliable and representative of water quality conditions at the time of sampling. The data comparison shows that as a screening tool, the ISE nitrate measurements were only reliable in isolated instances.

In order to have confidence in the nitrate ISE data, we would need to have significantly increased the nitrate ISE calibration frequency and observed better agreement between sonde measurements and quality control sample results. Unlike the DO probe verifications and recalibrations, which take only a few minutes to perform and cost very little, each nitrate ISE verification, recalibration and calibration check takes ½ to 1 hour to perform. Each sonde required up to 3 hours for testing and recalibration. The standards required for the calibration and QA/QC cost approximately a few hundred dollars. To significantly increase the frequency of the verification and recalibration appeared to be too time consuming and costly for the field screening program.

The potential sources of error in using this technology are pH variability in a stream; the presence of ion interference from other stream constituents; the stream sample contact time can be too brief; and, debris and membrane coating can cause misreading of the sensor. ISE stabilization during calibration often necessitated a "judgment call" on the part of the technician, as readings still drifted after ample calibration time had been provided. Solutions to potential sources of error will be evaluated in a future field program in which we field test some alternative technologies for this type of stream application. Technologies that incorporate flow injection or continuous flow delivery techniques with ISE analyses are under consideration. These techniques involve injection of a discrete or continuous stream sample into a continuously flowing reagent stream in a reaction manifold (or reverse flow injection) followed by ISE measurement.

References: Boyers, M.R. (1997). Aquatic Biology Investigation, Wissahickon Creek, PA Dept. of Environmental Protection; Conshohocken, PA; Clesceri, L.S., Greenberg, A.E., Eaton, A.D. (1998). Standard Methods for the Exam. Of Water and Wastewater, 20th ed., United Book Press, Inc., Baltimore, MD; Maxted, J.R., Dickey, E.L., Mitchell, G.M. (1995). The Water Quality Effects of Characterization in Coastal Plain Streams of Delaware, Delaware Dept. of Natural Resources and Environmental Control, Dover, Delaware.

Figure 1 : Dissolved Oxygen Results July - October, 1998

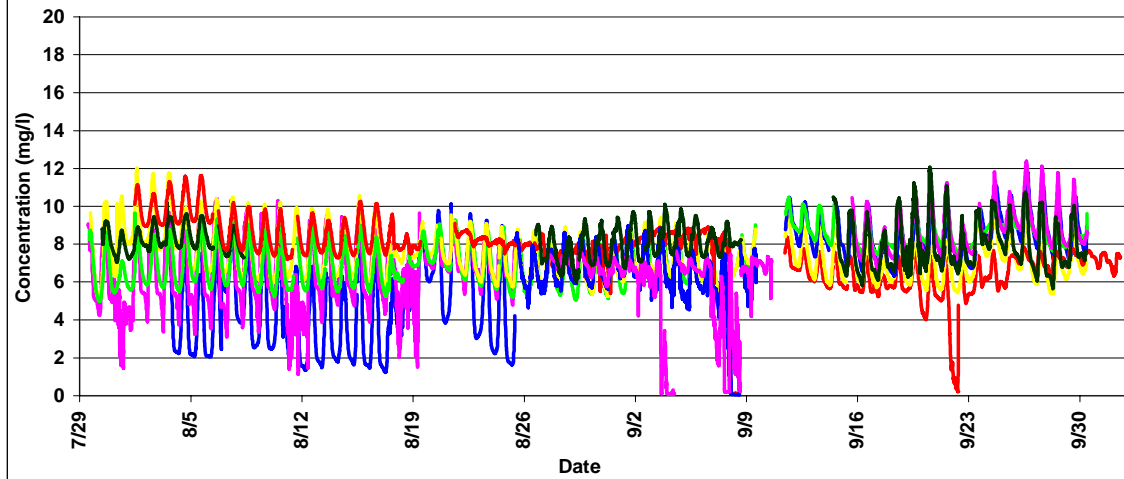


Figure 2: Dissolved Oxygen Measurements August - September 1998

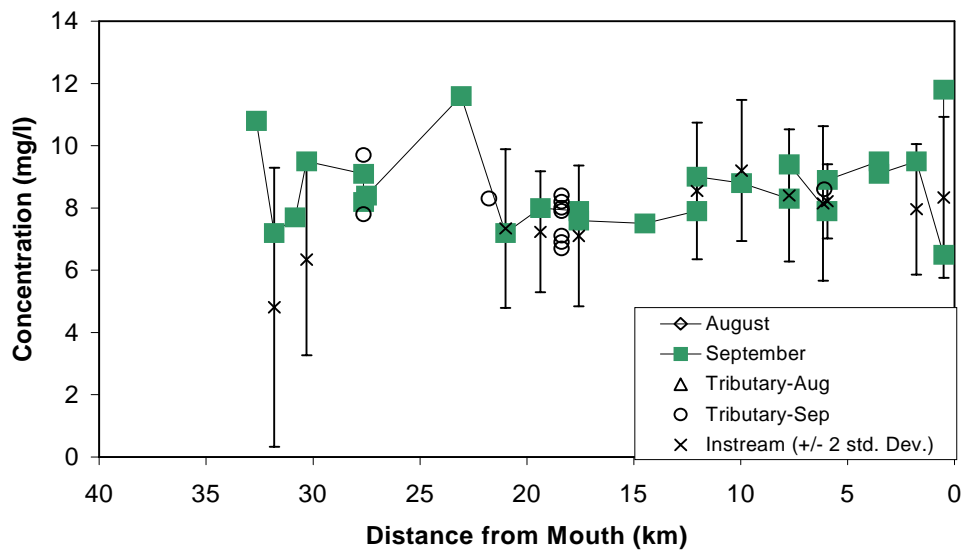


Figure 3: Dissolved Oxygen - L4 July 30 to September 9, 1998

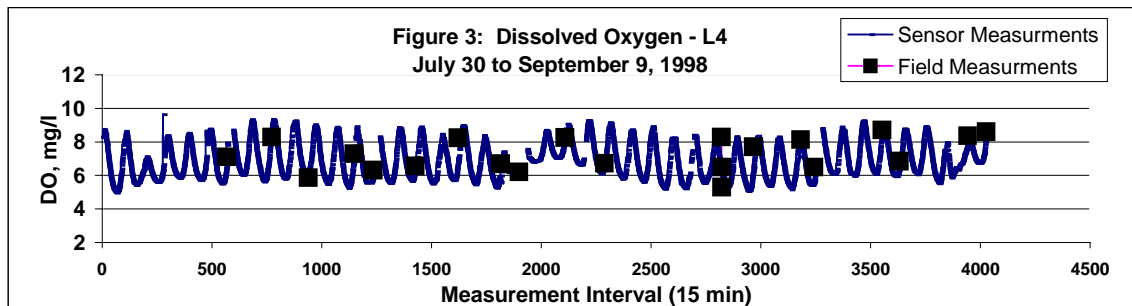


Figure 4: Nitrate as N - August & September 1998

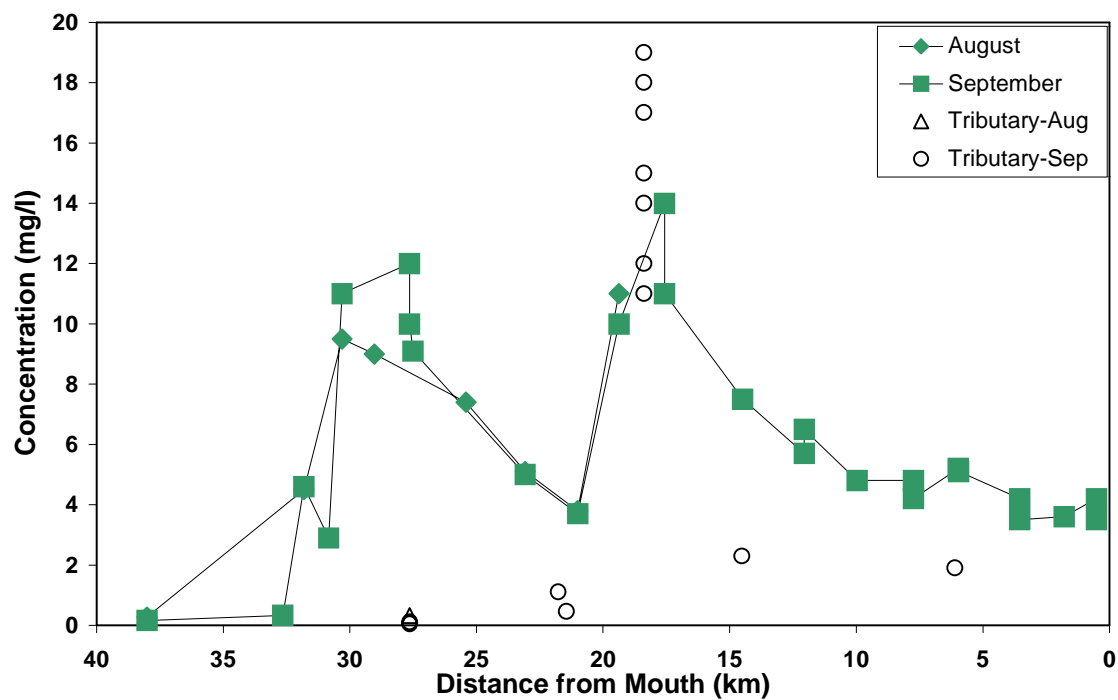


Figure 5: Ion Selective Electrode Nitrate Results
July - October, 1998

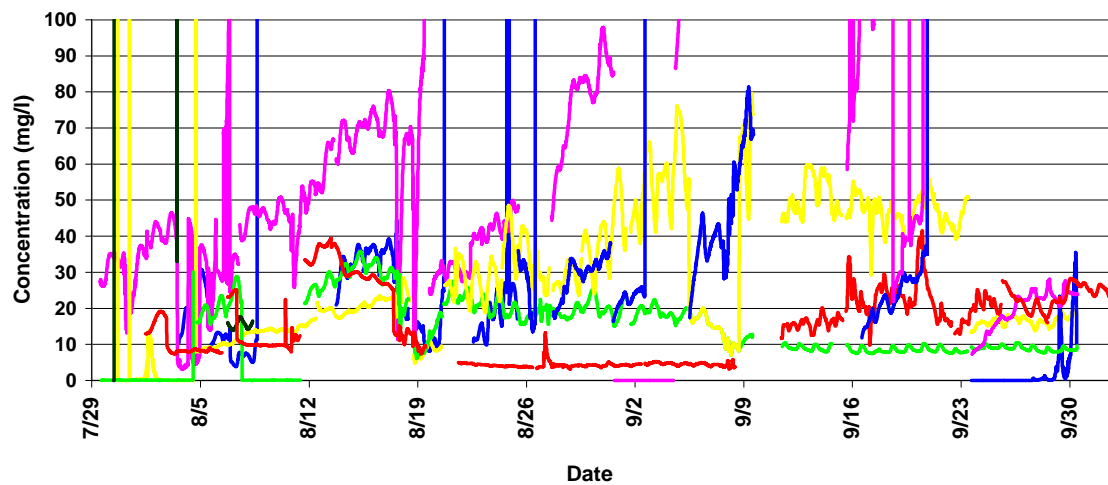
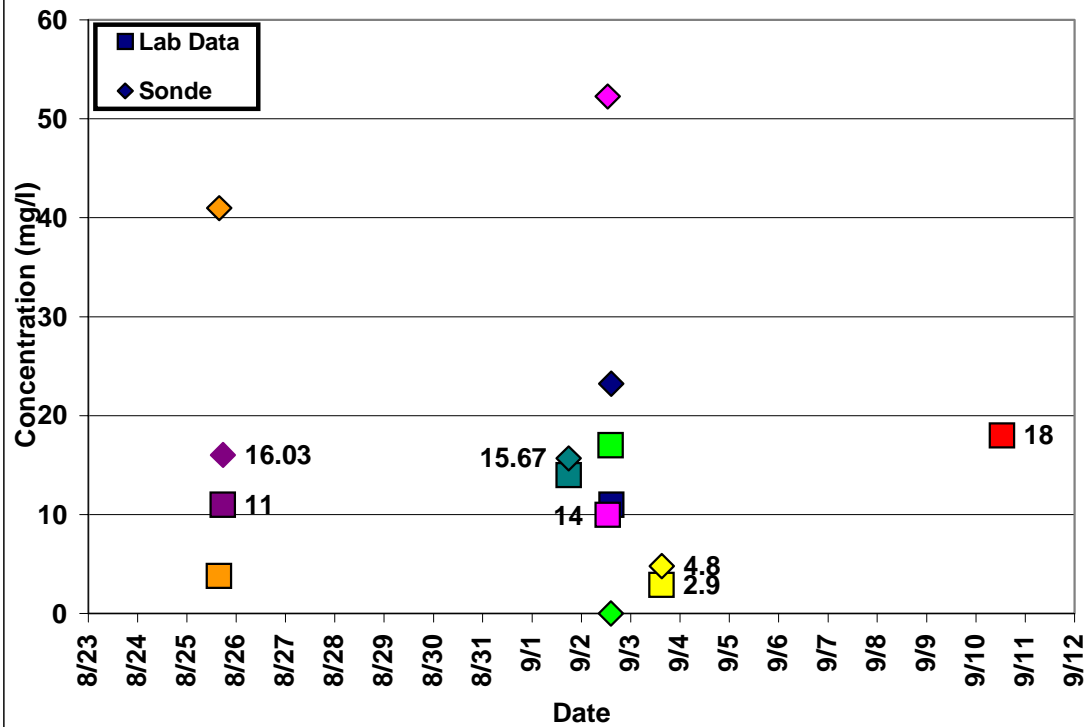


Figure 6: Laboratory Composite Sample Results and Sonde ISE Data - Nitrate



**Figure 7: L4 - Sonde Nitrate Measurements and Stream Samples
July 29, 1998 - September 9, 1998**

